[CONTRIBUTION FROM SOCONY-VACUUM LABORATORIES (A DIVISION OF SOCONY-VACUUM OIL CO., INC.) RESEARCH AND DEVELOPMENT DEPARTMENT]

Acylation Studies in the Thiophene and Furan Series. III. Natural and Synthetic Silica–Metal Oxide Catalysts

BY HOWARD D. HARTOUGH, ALVIN I. KOSAK[1] AND JOHN J. SARDELLA

It has previously been reported by two of the authors that iodine and hydriodic acid[2a] or zinc chloride[2b] catalyze the acylation of thiophene and furan with acyl anhydrides and halides. This paper deals with silica–metal oxide type catalysts such as naturally occurring clays, *e. g.*, montmorillonite clays and glauconite, and synthetic silica–metal oxide gels.

The bulk of this work was concentrated on an activated montmorillonite clay sold under the brand name of "Super-Filtrol." When this catalyst was employed in quantities ranging from 8.5 to 50 g. per mole of acylating agent, yields of 2-acetylthiophene ranging from 68 to 87% were obtained from thiophene and acetic anhydride.

Other clays investigated were attapulgus, glauconite,[3] and a synthetic zeolite, doucil. All had catalytic activity with the exception of the doucil. Attapulgus clay and a Hornerstown glauconite of high calcium content had very little activity but other glauconites of low calcium contents had high activity. Still higher activity of glauconites could be obtained by treating with sulfuric acid in the presence of ferrous sulfate (to maintain ferrous ion concentration in the catalyst) whereby the calcium contents were further reduced.

Synthetic silica–alumina gel catalysts such as Socony–Vacuum Bead Catalysts,[4] and Houdry cracking catalyst,[5] have shown high activity in catalyzing the acylation of thiophene with acetic anhydride. Yields of 2-acetylthiophene as high as 84% were obtained.

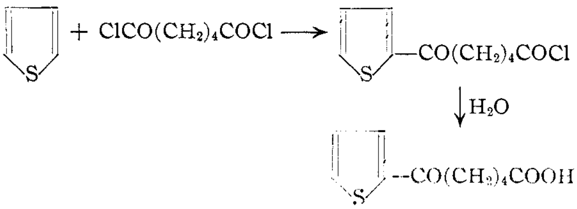
Other silica–metal oxide gels such as silica–zirconia, silica–thoria, and silica–hematite showed catalytic activity but in general they were inferior to silica–alumina compositions.

Silica gel, molybdic oxide and activated coconut charcoal failed to catalyze the acylation of thiophene. Alumina produced only a trace of ketone with thiophene and acetic anhydride. Chromia and beryllia on alumina each failed to show any catalytic action.

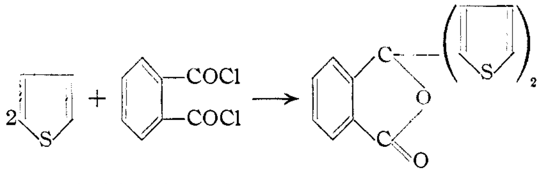
Comparison of catalyst activities indicated that the natural occurring clay, "Super-Filtrol," gave yields of 2-acetylthiophene from acetic anhydride and thiophene of the same order as the synthetic silica–alumina catalysts throughout a range of about 8 to 50 g. of catalyst per mole of acetic anhydride. When a sample of "Super-Filtrol" containing 13% by weight of water was used it was found that the yields were increased substantially over the freshly dried catalyst and the yields reached a maxima of 82% (compared to 68% yield with freshly dried catalyst) at 8.5 g. of catalyst per mole of acetic anhydride but fell off sharply above that amount due to decomposition of the anhydride with the water present. The dried catalyst gave yields that increased with increase of catalyst reaching a maximum yield at 87% with 50 g. of catalyst. The amount of water necessary to produce maximum activity of the clays has not been determined.

With the exception of benzoyl chloride, acid anhydrides are preferred over acyl halides because of substantially increased yields. This is consistent with results reported previously.[2] An excess of thiophene has been found to increase the yields (a one mole excess nearly doubles the yield over equimolar proportions) and the ease of handling the reaction mixture. Catalysts ground to pass a 60-mesh screen gave better results than 4 to 6-mesh pellets.

While no extensive study of the anhydrides of dibasic acids has been made, preliminary experiments indicate that more drastic conditions are required to produce acylation of thiophene. With adipyl chloride a 20% yield of 5-(2-thenoyl)-pentanoic acid was obtained.



Phthalyl chloride gave a 15% yield of 3,3-bis-(2-thienyl)-phthalide.



Fumaryl chloride and phosgene failed to condense with thiophene.

The 2-benzoylthiophene produced distilled to give an emerald green liquid that solidified upon cooling to a deep green crystalline product. This color has been noted previously in the distillation

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[2] (a) Hartough and Kosak, THIS JOURNAL, **68**, 2639 (1946); (b) **69**, 1013 (1947).

[3] For composition and occurrence of this marine deposit see Schneider, *J. Geol.*, **35**, 289–301 (1927); *C. A.*, **21**, 3584 (1927).

[4] Marisic, U. S. Patent 2,384,946, September 18, 1945.

[5] Peterkin and Shabaker, U. S. Patent, 2,232,727, February 25, 1941.

TABLE I

ACYLATION OF THIOPHENE AND FURAN

	Yield, %	Boiling point, °C.	Mm.	M. p., °C.	$n^{20}D$	Formula	Sulfur, % Calcd.	Sulfur, % Found
2-Acetylthiophene[a]	87	77[j]	4	10–11	1.5666			
2-Propanoylthiophene[b]	53	88[k]	7	......	1.5540			
2-Benzoylthiophene[c]	77	141–142	3	56.5–57[l]				
5-Chloro-2-acetylthiophene[d]	38	95–96	7	45–46[m]				
2-(2-Acetyl-5-thienyl)-pentane[e]	70	125–127	5		1.5321	$C_{11}H_{16}OS$	16.2	16.2
2-Crotonylthiophene (1-(2-thenoyl)-1-propene)[f]	22	109–116	5			C_8H_8OS	21.1	20.6
5-(2-Thenoyl)-pentanoic acid[g]	20			79–80		$C_{10}H_{12}O_3S$	15.02	14.99
3,3-bis-(2-Thienyl)-phthalide[h]	15			98.5–99		$C_{16}H_{10}O_2S_2$	21.48	21.76
2-Acetylfuran[i]	24	45–48	5	30–32				

[a] From two moles of thiophene, one mole of 95% acetic anhydride and 50 g. of "Super-Filtrol." [b] From one mole each of thiophene and propanoic anhydride and 15 g. of "Super-Filtrol." [c] From two moles of thiophene, one mole of benzoyl chloride and 20 g. of glauconite (raw, dried at 100°), reaction time was four hours. [d] From one mole of 2-chlorothiophene, 0.95 mole of 95% acetic anhydride, and 25 g. of "Super-Filtrol." [e] From 0.26 mole of 2-(2-thienyl)-*n*-pentane (obtained from P. D. Caesar, this Laboratory, data to be published later), 0.29 mole of 95% acetic anhydride and 15 g. of "Super-Filtrol." The semicarbazone melted at 167.5–168° and on analysis gave 16.3% nitrogen, calculated, 16.6%. [f] From 0.5 mole of thiophene, 0.5 mole of crotonyl chloride and 10 g. of "Super-Filtrol." 2,4-Dinitrophenylhydrazone melted at 183–185° dec. and on analysis gave 16.9% nitrogen, calculated, 16.9%. [g] From 0.27 mole of adipyl chloride, one mole of thiophene, and 5 g. of "Super-Filtrol"; reaction time was four hours. After washing with sodium hydroxide, the water layer was acidulated and the excess adipic acid leached out with hot water; the semi-pure product was recrystallized from ethyl acetate by addition of petroleum ether. The semicarbazone melted at 200–201° and on analysis gave 14.9% nitrogen, calculated, 15.6%. [h] From 1.5 moles of thiophene, 0.5 mole of phthalyl chloride and 25 g. of "Super-Filtrol"; reaction time was four hours. α,α-Di-(2-thienyl)-*o*-toluic acid, melting at 185–188° dec., was prepared by the method of Baeyer (ref. [n]) from the phthalide. Calcd. for $C_{16}H_{12}O_2S_2$: neut. equiv., 300. Found: neut. equiv., 310. Compound may be slightly impure. [i] From 0.5 mole of furan, one mole of 95% acetic anhydride and 5 g. of "Super-Filtrol" containing 13% water; reaction time three hours; temperature of reaction was 39–44°. [j] Steinkopf and Bauermeister, *Ann.*, **403**, 69 (1914), list b. p. of 91–92° at 13 mm. [k] Steinkopf and Schubert, *ibid.*, **424**, 8 (1920), list b. p. of 100–101° at 11 mm. [l] *Ibid.*, 19 (1920), lists m. p. of 56–57°. [m] Gattermann and Romer, *Ber.*, **19**, 693 (1889), list m. p. of 52° but repeated recrystallizations of our product did not give sample that melted above 46°. [n] Baeyer, *ibid.*, **12**, 644 (1879).

of 2-*o*-toluylthiophene.[6] Attempts to decolorize with activated charcoal in alcohol produced a deepening of the green coloration. It was noted that this color develops during the vacuum distillation and is not encountered if the crude reaction mixture is not distilled, but is purified according to other conventional methods. No attempts have been made to isolate this color body, but it can be concentrated in the first crop of crystals in the recrystallization of the 2-benzoylthiophene from ether–petroleum ether mixtures. The green color can be diminished by recrystallization from ASTM naphtha.

Vapor phase acylations of thiophene with acetic anhydride over pelleted "Super-Filtrol" and silica–alumina at 225–300° have not been very successful. Yields of 20% were generally obtained in a single pass but the conversions were low because of the tendency of thiophene to undergo ring rupture with the evolution of hydrogen sulfide at these temperatures.

The catalysts lose their activity rapidly and if reused the yield drops to about 50% of the original. The catalysts may be reactivated by treatment at 550° for three hours in a muffle furnace. Acylation of furan with these catalysts was not so fully investigated since the yields were much inferior to those previously reported.[2] The highest yield of 2-acetylfuran obtained was 24%.

Experimental

With the single exception of the work on acetic anhydride and thiophene, experiments were made to investigate the versatility of the reaction and in some cases the optimum conditions were not observed. Therefore, the yields listed below in the preparations might be increased with further study.

Preparation and Pretreatment of Catalysts.—Each catalyst with the exception of glauconite was ground to pass a 60-mesh screen and dried at 550° for three hours in a muffle furnace. Glauconite was dried at 100° to remove surface water since the ferrous iron is converted to ferric at 550° with subsequent loss of catalytic activity.

"Super-Filtrol" was obtained from the Filtrol Corp. and was ground to pass a 200-mesh screen. When obtained this material usually contains 5–15% water. A sample containing 13% water was found to have higher activity than a sample dried at 550°.

General Acylation Procedure.—A mixture of thiophene, acylating agent and catalyst was stirred at the reflux temperature for six hours, cooled, the catalyst filtered off, and the liquid products fractionated under vacuum in a 10-plate fractionating column. Crystalline products were distilled in a suitable apparatus. When acyl halides were used the reaction mixture was washed with 10% sodium hydroxide until neutral.

Acknowledgments.—The authors wish to thank Dr. Darwin E. Badertscher for his advice and interest in this problem; Miss Josephine Sindoni and Miss S. Gretchen Webster for their coöperation in carrying out some of the laboratory preparations; Mr. Rowland C. Hansford who furnished all of the synthetic silica–metal oxide gels for this work; and the Hungerford–Terry Corporation of Clayton, N. J., for samples of glauconite.

Summary

Naturally occurring clays of the montmorillonite family, glauconite, and synthetic silica–metal

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(6) Steinkopf, *Ann.*, **412**, 349 (1917).

oxide gels have been found to promote the acylation of thiophene and furan.

Yields of 2-acetylthiophene as high as 87% are reported when a montmorillonite clay was employed with two moles of thiophene and one mole of acetic anhydride. Similarly, synthetic silica–alumina gel catalysts have given yields as high as 84%. 2-Benzoylthiophene has been prepared in yields of 94% from the action of a montmorillonite clay on benzoyl chloride and thiophene. 2-Acetylfuran has been obtained in 24% yields from acetic anhydride and furan. Due to the lower yields, no extensive study of the acylation of furan was made.

In general, the acid anhydrides are preferred to the acyl halides. With thiophene higher yields are obtained with the anhydrides. With furan no acylation has been noted with acyl halides.

3,3-bis-(2-Thienyl)-phthalide has been prepared from phthalyl chloride and thiophene in 15% yields. Adipyl chloride and thiophene yielded 20% of 5-(2-thenoyl)-pentanoic acid.

PAULSBORO, N. J. RECEIVED AUGUST 10, 1946

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXVII. The Conductance of Several Quaternary Ammonium Salts in Ethylene Chloride at 25°[1]

BY WALTER E. THOMPSON[2] AND CHARLES A. KRAUS

I. Introduction

The results of conductance measurements with a considerable number of electrolytes in ethylene chloride have formed the subject of several communications from this laboratory. The present paper extends our knowledge of the effect of the constitution and size of anions upon the electrolytic properties of their salts. In particular, the behavior of the following ions, in the form of their tetra-alkylammonium salts, has been investigated: chloride, bromide, thiocyanate, acetate, chloroacetate and borofluoride.

Fowler and Kraus[3] have developed a method of approximating limiting ion conductance values from conductance measurements alone. In view of the importance of ion conductances, it seemed desirable to obtain an independent check on Fowler's values. For this purpose, octadecyltrimethylammonium octadecylsulfate was employed. In composition and structure, the two ions are very similar and are of a type differing greatly from those used in Fowler's investigation. Assigning equal conductance values to the two ions of this salt, we have obtained limiting ion conductances in favorable agreement with those obtained by Fowler. Fowler's measurements with tetrabutylammonium triphenylborofluoride and Mead's[4] with tetrabutylammonium picrate were repeated and their results confirmed.

The effect of small additions of a highly polar substance, such as methyl alcohol, on the electrolytic properties of three quaternary ammonium salts has been studied.

II. Experimental

Apparatus and Procedure.—The methods employed in the purification of the solvent, in the preparation of the solutions and in the measurement of the resistances have been described fully in previous communications. Densities of solutions containing polar molecules were determined with a Westphal balance, while viscosity measurements were carried out in accordance with standard procedure. All measurements were carried out at 25 ± 0.01°.

Materials.—Pure methanol was obtained in the usual manner by treatment with calcium oxide. Although its specific conductance was approximately 3×10^{-6}, the values for the mixtures with ethylene chloride were less than 0.1% of the total conductance of the most dilute solutions.

Tetramethylammonium picrate which had been used in previous conductance measurements was available.

Tetraethylammonium chloride was recrystallized from ethylene chloride and the bromide from mixtures of acetone and alcohol; both decomposed without melting.

Tetraethylammonium borofluoride was prepared by Mr. G. W. Moessen, as described by Witschonke[5]; m. p. 235°. Methyltri-*n*-butylammonium thiocyanate was provided by Dr. L. E. Strong[6]; m. p. 101°.

Tetra-*n*-butylammonium acetate was prepared by neutralizing a solution of the hydroxide with acetic acid. This salt, like the corresponding chloroacetate, is prepared with great difficulty because of its great hygroscopicity. After evaporation of the solution on a steam-bath, the product was dried for two weeks over phosphorus pentoxide at pressures below 0.001 mm. It was then recrystallized from *n*-butyl chloride from which the last traces of alcohol had been removed by successive distillations from calcium chloride and phosphorus pentoxide. The salt was dissolved at 60° and about 15% crystallized out on cooling to the temperature of an ice–salt mixture. Additional crystals of higher purity were obtained by adding dry pentane to the cold solution. The last traces of butyl chloride were removed by means of a mercury vapor pump. An accurate melting point of this salt was difficult to obtain because of its hygroscopic properties; m. p. 118 ± 2°.

Tetra-*n*-butylammonium chloroacetate was prepared like the acetate by interaction of the base and acid in aqueous solution. This salt is even more hygroscopic than the acetate and is more difficult to crystallize. The

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[1] This paper is based on a portion of a thesis presented by W. E. Thompson in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1941.

[2] University Fellow at Brown University, 1939–1940; Metcalf Fellow, 1940–1941.

[3] Fowler and Kraus, THIS JOURNAL, **62**, 2237 (1940).

[4] Mead, Fuoss and Kraus, *Trans. Faraday Soc.*, **32**, 594 (1936).

[5] Charles R. Witschonke, Thesis, Brown University, 1941.

[6] Lawrence E. Strong, Thesis, Brown University, 1940.